CHARACTERIZATION AND STUDY OF ADSORPTION OF METHYLENE BLUE DYE USING ACTIVATED CARBON

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In partial fulfilment of the requirements of

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By

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CERTIFICATE

This is to certify that the thesis entitled, "***CHARACTERIZATION & STUDY OF ADSORPTION OF METHYLENE BLUE DYE USING ACTIVATED CARBON"*** submitted by ***Debi Prasad Samal,*** bearing ***Roll No.-110CH0108***, in partial fulfilments for his requirements for the award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela is prepared by him under my supervision and guidance.

DATE:

Dr. Susmita Mishra

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NOMENCLATURE

°C : Degree Celsius

BET : Brunnauer Emett Teller

nm : Nanometer

HCl : Hydrochloric acid

NaOH : Sodium hydroxide

UV : Ultra-violet

ASTM : American Society for Testing and Materials

M : Moisture content

A : Ash content

VM : Volatile matter content

q_e : amount of substance adsorbed per unit mass of adsorbent

C_o : initial concentration of methylene blue

C_e : equilibrium concentration at time

ABSTRACT

Characterization of activated carbon was studied extensively. Proximate Analysis, SEM, BET, Porosity, pH, Iodine No, solubility were some of the characterization techniques which was applied minutely on activated carbon prepared from coconut shell in order to predict its Surface area, Porosity, Surface Topography, pH etc. .

Activated Carbon are extensively used in the abatement of hazardous contaminants, treatment of municipal & industrial waste water, as catalyst or catalyst support in medicine, & the recovery of valuable metals because it is specially treated to create a highly developed internal pore structure & thus this pore structure is responsible for the superior performance of activated carbons.

My work focused on removal of methylene blue dye using commercial activated carbon. Using activated carbon the removal of methylene blue dye was studied by changing different parameters such as initial pH, initial adsorbent dosage, initial dye concentration & contact time. Finally the experimental data were fitted into both Langmuir & Freundlich isotherms.

Thus the given activated carbon prepared from coconut shell could be used extensively in removal of methylene blue dye from waste water.

Key word: Surface Area, Isotherms, effluents, contact time, pore structure, catalyst.

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

Presence of industrial dye in the effluent has released a voluminous amount of toxicity to the water system that has affected the human beings as well as the flora and fauna.

Dyes are used extensively in various industries such as textiles, rubber, plastics, printing, leather, cosmetics, etc., and also in production of coloured products. About 7 X 10^5 dyes are produced annually in the global market. It is estimated that about 2% of these dyes are discharged into the water system with most of the sources generated from textile industries.
Dyes affect the penetration of sunlight into the water bodies and thus interfere with the growth of bacteria and hinder photosynthesis in aquatic plant. It poses a serious threat to mankind and water quality, thereby is a matter of vital concern. It causes acute and chronic effects on exposure to human skins such as allergic, dermatitis, skin irritation, cancer, mutation etc. Among the various treatment methods such as photo-catalytic degradation using UV TiO_2, sono-chemical degradation, Fenton biological treatment, biodegradation, integrated chemical – biological process, electrochemical process, adsorption process, chemical coagulation flocculation degradation process etc. have been explored to remediate these dyes in the waste water. Among the various techniques available for its remediation adsorption technique has been proved to be most effective. Adsorption is preferred over other processes due to possible regeneration, sludge free operation and recovery of the sorbet.

Adsorption is an unit operation process which refers to attachment of molecules onto the surface. It is based on the fact that some solids preferentially adsorb other solute from the solution onto their surfaces. Dyes are particularly removed using various adsorbents. Many such adsorbents such as orange peel, neem seed, oil cakes, date palm, olive shell, charcoal etc has been explored for its removal. However activated carbon has shown significant removal properties with respect to other adsorbents. It is a versatile adsorbent with high porosity and surface area. Among the various types of dyes removed activated carbon has selectively used for removal of methylene blue dye which has been extensively used in the textile industry.

Thus the basic objective of our study is to observe the characteristics properties of the commercial activated carbon and find the influence of process parameters such as pH, adsorbent dosage, contact time and adsorbate concentration on removal capacity of methylene blue.

1.1 OBJECTIVE

The purpose of this project work is:

- To study the characteristics property of the activated carbon
- To study the influence of various process parameter on the adsorption phenomena and verify the reported data with different adsorption isotherms.

1.2 SCOPE

Study the characteristic properties of activated carbon

- pH
- solubility
- bulk density
- methylene blue no
- BET surface area
- Iodine no

Study the effects of various experimental parameters on adsorption like

- E f f e c t of contact time
- E f f e c t of pH
- E f f e c t of adsorbent dose
- E f f e c t of initial concentration of methylene blue

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

Methylene Blue ($C_3H_{18}ClN_3S$) is a monovalent cationic dye. Molecular weight of is 373.9. MB is a basic dye & got many utilities in terms of dyeing of silk, leather, paper & cotton as well as production of ink. The discharge of MB is a great threat for both toxicological & aesthetical reasons impede light penetration & are toxic to supply food chain for organisms.

Since it has a synthetic origin & complex organic aromatic structure; hence, they are inert & difficult to bio-degrade when discharged into the water. The various treatment options have been explored and adsorption technique has been widely welcomed for the removal of methylene blue dye from the effluent. The substance onto which liquid molecules get adsorbed is called adsorbent & the liquid molecules that get adsorbed onto the adsorbent are known as adsorbate. The process of adsorption is divided into two categories depending on type of forces involved between adsorbent & adsorbate.

a) Physiorption
b) Chemisorption

It involved intermolecular force of attraction. It is based on the fact there is a concentration gradient of adsorbate in solution & adsorbent so that adsorbate migrates from solution into the pores of adsorbent to reach the point of maximum force of attraction & thus get adsorbed. It involves chemical bonding between the adsorbent & adsorbate molecule In general most of the solids has a property to adsorb the solute from solution but few of them are actually used commercially. Among these MOF, Activated carbon, Silica gel, activated alumina are used extensively.

The most desirable property or the pre requisite for a good adsorbent is that it should have large surface area i.e surface area per unit mass. Bulk of this surface area is because of presence of internal pores of different sizes that can be classified into three categories i.e,

a) micropore < 2 nm
b) mesopore 2-50 nm
c) macropore >50 nm

The adsorbent are quite specific in ability to adsorb adsorbate depending on size of pore

& size of molecules being adsorbed.When an adsorbate comes in contact with adsorbent adsorption takes place & after a long time it the adsorption process reaches to a equilibrium state. The adsorption isotherm can have different shape which is based on adsorbent, adsorbate & adsorbent-adsorbate interaction.

For the production of activated carbon, a wide variety of raw materials have been used over the years. Extensive studies have been undertaken by various scholars and researchers for the synthesis and characterization of adsorbents from different agricultural based precursors.

The following table gives a brief review of the various raw materials that have so far been used for the production of activated carbons.

Table 1: List of raw materials which have been used for the production of activated carbon

Raw materials	**Authors**
Walnut shells	Aygün A. ,Yenisoy-Karakaş S. [9]
Coir pith	Kavitha D. , Namasivayam C. [10]
Apricot stones	Aygün A. , Yenisoy-Karakaş S. [9]
Almond shell	Aygün A. ,Yenisoy-Karakaş S. [9]
Hazelnut shell	Aygün A. ,Yenisoy-Karakaş S. [9]
Silk cotton hull	Kadirvelu K., Kavipriya M. [11]
Maize cob	Kadirvelu K., Kavipriya M. [11]
Coconut coir dust	Macedo J. S., Júnior N. B., Almeida L. E. [12]
Peach stones	Caturla F., Molina-Sabio M., Rodríguez-Reinoso F. [13]
Sugarcane bagasse	Girgis B.S., Khalil L.B., Tawfik T.A.M. [14]

In 2005 B.H.Hameed, A.T.M.Din and A.L.Ahmad carried out adsorption of methylene blue by bamboo-based activated carbon. Bamboo was used to make activated carbon by physiochemical activation with potassium hydroxide and carbon dioxide. Adsorptiobn models and kinetic studies were also conducted and it was found that pseudo-second-order model best described the process [7].

In 2007, R.A.Shawabkeh and E.S.M. Abu-Nameh performed study of adsorption of phenol and Methylene Blue by activated carbon from pecan shells. Activated carbon was prepared from pecan shells by chemical activation with phosphoric acid. Then it was treated with sodium dodecyl sulfate to prepare the surface for adsorption. The results indicated good removal of phenol and Methylene Blue dye by pecan shells.[17]

The removal of methylene blue using treated and untreated activated carbon was investigated by Yasin, Hussein and Ahmad{yaminuitm}. The effects of various experimental parameters like contact time, pH of the solution and adsorbent dosage were studied. It was found that the amount of methylene blue removal increased with the increase in contact time, solution pH and amount of adsorbent used. The data obtained best fitted the Langmuir isotherm plot. [18]

The adsorption of methylene blue onto dehydrated wheat bran (DWB) was investigated by Ozer A and Dursun G., at temperatures (25-45 °C), initial methylene blue (MB) concentrations (100-500 mg/L) and adsorbent dosage at the given contact time for the removal of dye. The pseudo first order and pseudo second order kinetic model were applied to the data and it was found that pseudo second order best described the data obtained.[19]

In another instance, jute fibre was used to prepare activated carbon using phosphoric acid. It was found that at a fixed carbon concentration, the decrease in particle size increased the dye uptake and decreased the equilibrium time. The per cent adsorption decreased with increase in the initial methylene blue concentration, but the actual amount of methylene blue adsorbed per unit mass of carbon increased with increase in methylene blue concentration. The Langmuir equation gives an accurate description of the experimental data.[6]

The adsorption of methylene blue (MB) from aqueous solution using a low-cost

adsorbent, rejected tea (RT), was studied by batch adsorption technique. The adsorption experiments were carried out under different conditions of initial concentration (50-500 mg/L), solution pH 3-12, RT dose (0.05-1g) and temperature (30-50 °C). The equilibrium data were fitted to Langmuir and Freundlich isotherms and the equilibrium adsorption was best described by the Langmuir isotherm model with maximum monolayer adsorption capacities found to be 147, 154 and 156 mg/g at 30, 40 and 50 °C, respectively. . The results suggested that RT has high potential to be used as effective adsorbent for MB removal.[7]

Activated carbon prepared from non-wood forest product waste (rattan sawdust) has been utilized as the adsorbent for the removal of methylene blue dye from an aqueous solution. The rattan sawdust was collected from a local furniture factory.

Adsorptioisotherm

Adsorption is generally described through isotherms, that are amount of adsorbate on the adsorbent as a function of pressure (for gases) or concentration (for liquids) at a constant temperature.

Freundlich isotherm:

It is an adsorption isotherm which relates concentration of solute on the surface of the adsorbent to the concentration of the solute in the liquid with which it is in contact. This model assumes that adsorption takes place on heterogeneous surface.

The linear form can be written as:

$\log qe = \log k_f + (1/n) * \log C_e$

Where, k_f and n (dimensionless constants) are the Freundlich adsorption isotherm constants, which indicate the capacity and intensity of the adsorption, respectively.

Langmuir isotherm:

It relates the adsorption of molecules on a solid surface to gas pressure or concentration of a medium above the solid surface at a fixed temperature. It is based upon the fact that adsorption process occurs in monolayers.

The linear form of Langmuir expression:

$1/q_e=1/Q_o+ 1/(bQ_oC_e)$

Where Ce is the equilibrium concentration of dye solution (mg/L), qe is the equilibrium capacity of dye on the adsorbent (mg/g), qo is the monolayer adsorption capacity of the adsorbent (mg /g), and b is the Langmuir adsorption constant (L/mg) and is related to the free energy of adsorption.

CHAPTER 3

MATERIALS AND METHODS

3. MATERIALS AND METHODS

3.1 Characterization of raw activated carbon

The following characteristic properties of activated carbon were studied

3.1.1 Proximate Analysis-

ASTM defines proximate analysis as the determination by prescribed methods of moisture, volatile matter, ash & fixed carbon. The proximate analysis of the given activated carbon sample will be followed by the procedure given below.

a) Moisture Content-

A small amount of the sample was put in a petri-dish or crucible, covered with a lid & weighed using a weighing balance. The crucible was placed in the hot air oven at 105^{o} C with its lid removed & dried for 1.30 hrs. The crucible was taken out, immediately covered with the lid, cooled in a dessicator & weighed.

M=100(B-F)/(B-G)

Wt of empty petri-dish=42.185 gm=G

Wt of empty petri-dish + Activated carbon sample (before heating)=B=52.185 gm

Wt of empty petri-dish + moisture free sample (after heating)=F=51.263 gm

% of moisture content (M)=9.22

b) Ash content

The crucible was ignited in the muffle furnace at 750$\pm$ 25^{o}C for 1.5 hours. The crucible was placed in the dessicator, cooled to room temperature & weighed. A known amount of the sample which was dried in the hot air oven at 150 ^{o}C for 3 hours was put in the crucible & the crucible was placed back in the muffle furnace at 750$\pm$25 ^{o}C for 1.5 hours. The crucible was taken out of the furnace, placed in the dessicator, cooled to room temperature & weighed.

A=100(F-G)/(B-G)

Wt of empty silica crucible=G=21.433 gm

Wt of empty crucible + activated carbon sample (before heating)=B=22.433 gm

Wt of empty crucible + ash (after heating)=F=21.448 gm

% of ash content=1.5

c) Volatile matter content

A known amount of sample was put in the crucible. The crucible was placed in a muffle furnace at $920\pm10^{o}C$, covered with lid, & placed for exactly 7 minutes. The crucible was taken out, allowed to cool & weighed.

VM=100(100(B-F)-M(B-G))/((B-G)(100-M)

Wt of empty crucible with lid=G=14.003 gm
Wt of empty crucible + lid + sample(before heating)=B=15.003 gm
Wt of empty crucible + lid + sample (after heating)=F=14.844 gm
M=Moisture content in %
% of volatile matter content=7.358

d) Fixed carbon

% of fixed carbon=100-(M+A+VM) = 81.922

3.1.2 SCANNING ELECTRON MISCROSCOPE

SEM is a type of microscope which uses a beam of highly energetic electrons to scan a sample. & produce its image. It consists of a electron gun which acts as an source for electrons. The electron beam is focussed by a pair of condenser lenses made of magnets which are capable of bending the path of electrons. Sample to be analyses is placed in the sample chamber. The electron beam strikes the sample gets decelerated & produces a variety of diffracted backscattered electrons, protons, visible light & heat. The secondary electrons are picked up by the electrons & produces images of the object's surface on the monitor. The entire operation takes place in the a vacuum chamber.

The activated carbon can be analysed in a SEM to visualize the porous structure. The magnification is analysed & adjusted so as to get a clear picture.

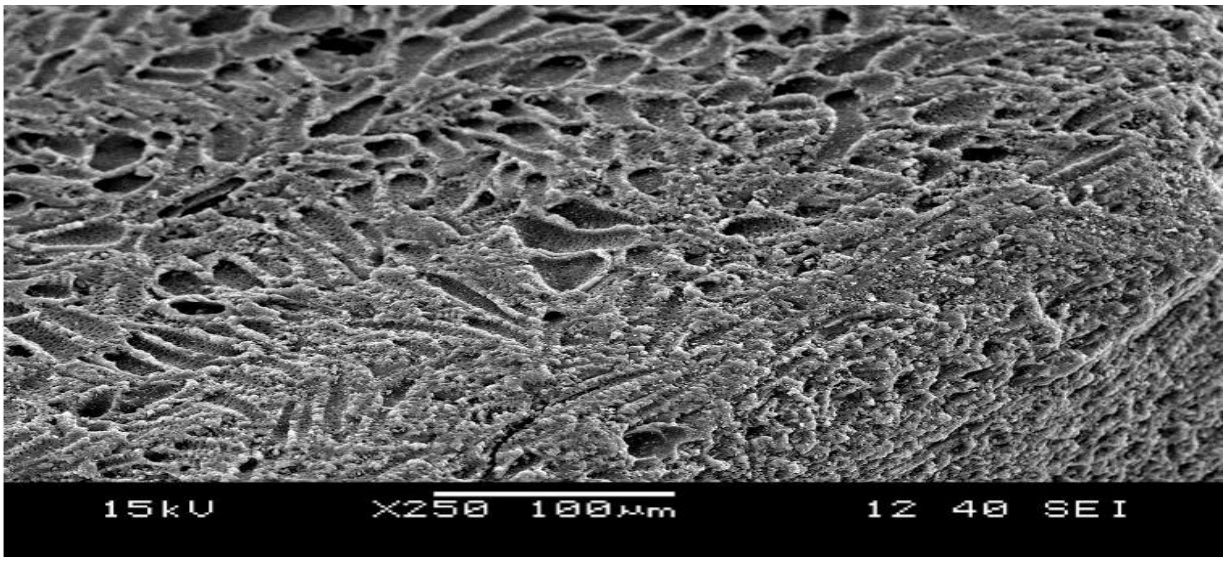


Figure-1. a) SEM image of raw modified activated carbon at x 250 zoom

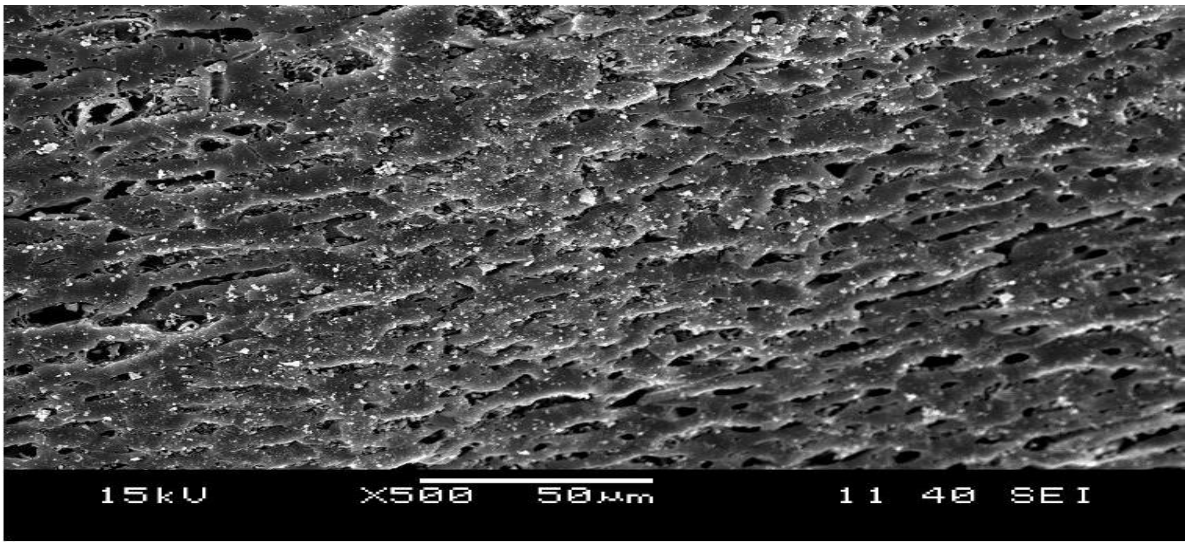


Figure-1 **b) SEM image of raw modified activated carbon at x 500 zoom**

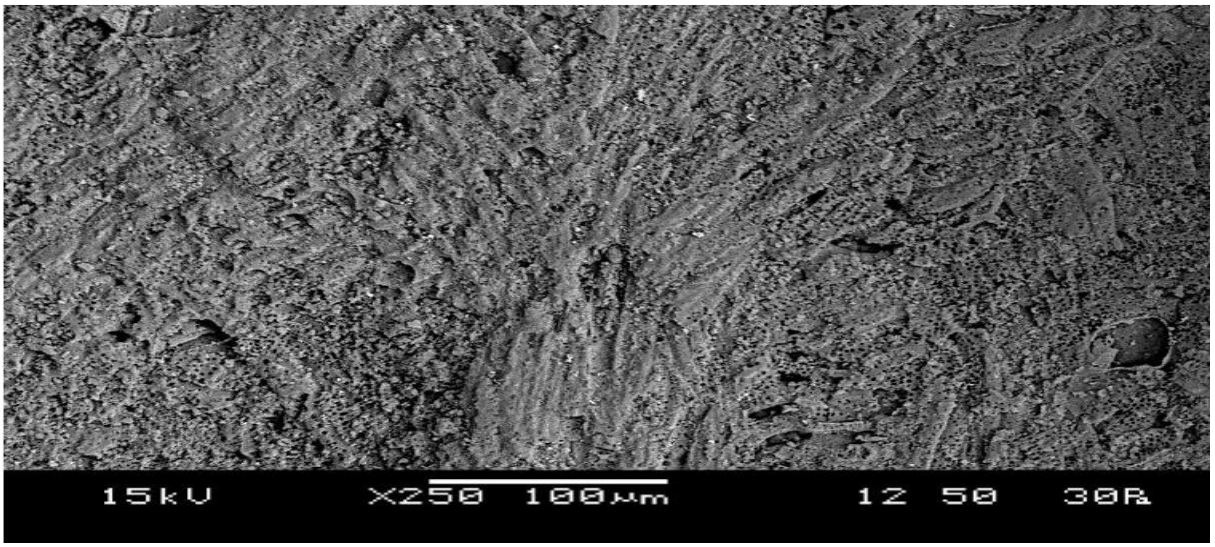


Figure-1. a)BSM image of raw modified activated carbonat x 250 zoom

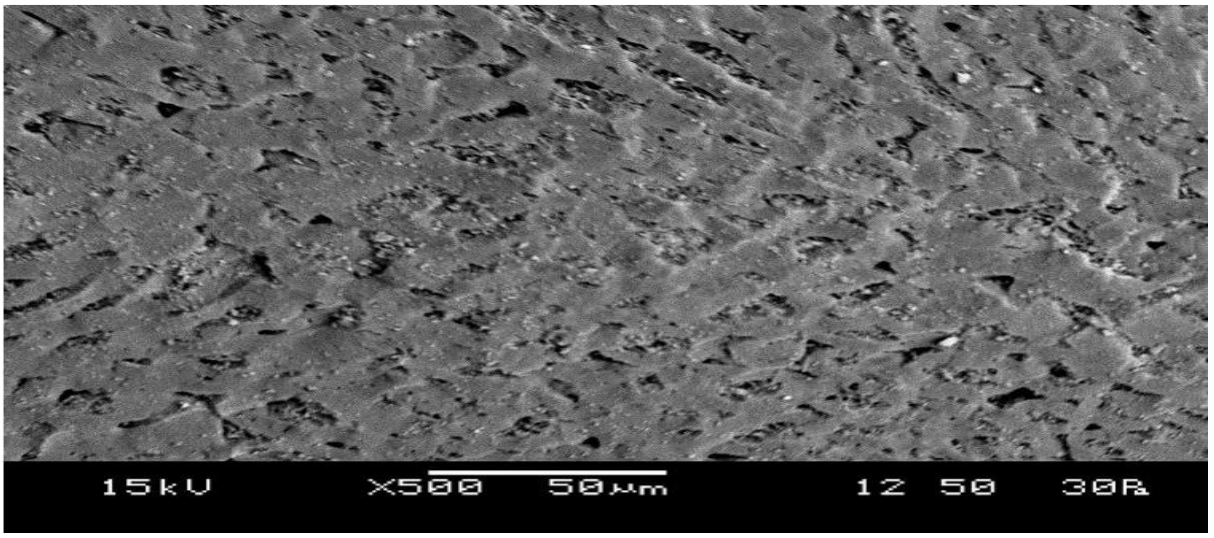


Figure-1. b)BSM image of raw modified activated carbon at x 500 zoom

3.1.3 IODINE NUMBER

Iodine number is the milligrams of iodine adsorbed by 1 gm of activated carbon from a 0.1N iodine solution when the equilibrium iodine concentration is exactly 0.02N. Iodine number is a measure micro-pore content of the activated carbon. A higher iodine number indicates higher micro- porosity of the sample.

ASTM D4607-94(2006) gives the standard procedure for the determination of the iodine number of the activated carbon. 0.7-2 g of dried activated carbon was mixed with 10 ml of 5% by weight & swirled in a conical flask until the activated carbon was wetted. The flask was boiled for 30 sec by placing it on a hot plate. The content of the flask was

cooled to room temperature & 100 ml of 0.1 N iodine solution was added on it. The flask was shaken vigorously for 30 sec. The contents were filtered through a filter paper. Initial 20-30 ml of the filtrate was discarded & the remaining filter was collected in a clean beaker. 50 ml of this filtrate was titrated against 0.1 N sodium thio-sulphate solution until yellow colour just disappeared. 1 ml of starch solution was added & titration was carried out till blue colour was just disappeared.

The iodine no was found out to be 986 mg/g.

3.1.4 pH

pH was determined using the standard method ASTMD 3838-80, 1g activated carbon sample was put in a conical flask & 100 ml of distilled solution was added into it. The mixture was stirred for 1 hour, pH readings are taken out using pH meter.

pH was 10.9 which shows basic in nature.

3.1.5 METHYLENE BLUE NUMBER

Methylene blue number is defined as the milligrams of methylene blue dye adsorbed by 1g of dried activated carbon. It is a measure of the mesopore content of the activated carbon.

1200 mg/l methylene blue stock solution was prepared. The sample was diluted to give solutions of 5 different concentrations. A standard calibration curve was prepared by measuring the absorbance at 664 nm. A known concentration solution was prepared from the stock solution and a known amount of activated carbon was put into it. The flask was placed in a shaker at 25 ^{0}C for 24 hours at 115 rpm. The absorbance of the resulting solution was measured at 664 nm and the concentration was calculated from the calibration plot.

3.1.6 BET SURFACE AREA

The BET surface area is one of the parameters that determine the absorption capacity of the activated carbon. Higher surface area implies more availability of surface for adsorption hence better adsorption capacity.

BET stands for Brunauer, Emmett and Teller-the men who proposed a theory to measure the surface area of solid particles like porous powders. The basic principle involved is the adsorption of gas molecules to the surface of the solid whose surface area is required. From the area of each molecule, the whole area of the solid can be calculated.

BET theory is based on multilayer adsorption with the following assumptions

1. Gas molecules can be physically adsorbed on the solid surface and form infinite layers.
2. There is no interaction between the layers
3. Langmuir theory is applied to each layer

The BET equation is given by:

$1/v\ [(P^0/P)-1] = (c-1)\ (P/P^0)/\ (v_m c) + 1/\ (v_m c)$

P^0= Saturation pressure of the adsorbate

P= Equilibrium pressure of the adsorbate

v= Volume of gas adsorbed

v_m= Volume of gas adsorbed in the monolayer

c= BET constant given by exp (E1-EL)/RT

E1= Heat of adsorption for the first layer

EL= Heat of adsorption for higher layers

A plot of $1/v\ [(P^0/P)-1]$ v/s (P/P^0) is obtained from the BET analysis. From the slope and intercept of the line, v_m and c are obtained. Surface area S of the solid sample is given by

$S= (v_m Ns)/ (VX)$

N= Avogadro's number

s= adsorption cross-section of the gas being adsorbed

V= molar volume of the gas being adsorbed

X= mass of the adsorbent

A small amount of the sample was taken in the tube and the tube was placed in a dewar containing liquid nitrogen. Initially the sample was degasified to remove the impurities and gases. Then gaseous nitrogen was passed through the sample and based on adsorption of the gas, the surface area of the sample was calculated.

3.2 CHEMICAL

Methylene blue dye, chemical formula, $C_{16}H_{18}N_3ClS$ and molecular weight of 319.5 was used for the initial adsorption experiments. Other chemicals such as NaOh and HCl were used for preparing solutions of varying pH. The adsorbent taken as activated carbon prepared from coconut shell. The chemicals & adsorbent were provided by the department laboratory.

3.3 INSTRUMENTION

A hand shaker was used for all the adsorption experiments. A UV-ray spectrophotometer was used to determine the absorbance. The pH meter was used to measure the pH of solution. Glass wares & conical flask were used to handle the solutions. A meter balance was used to weigh the samples. Pipette was taken taken in transferring the solution into the test tube to record the adsorbance of solution.

Figure 3 The hand shaker used for the experiments.

Figure 4 glasswares used to handle the chemicals and carryout the experiment

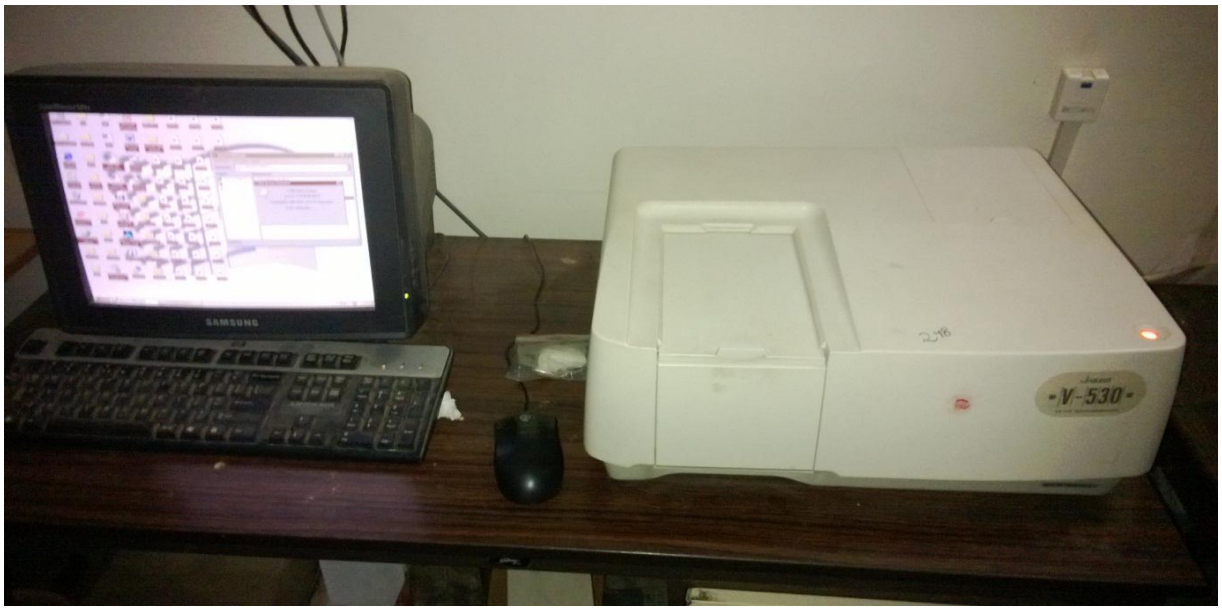


Figure 5 the UV-spectrophotometer used for determining the % absorbance.

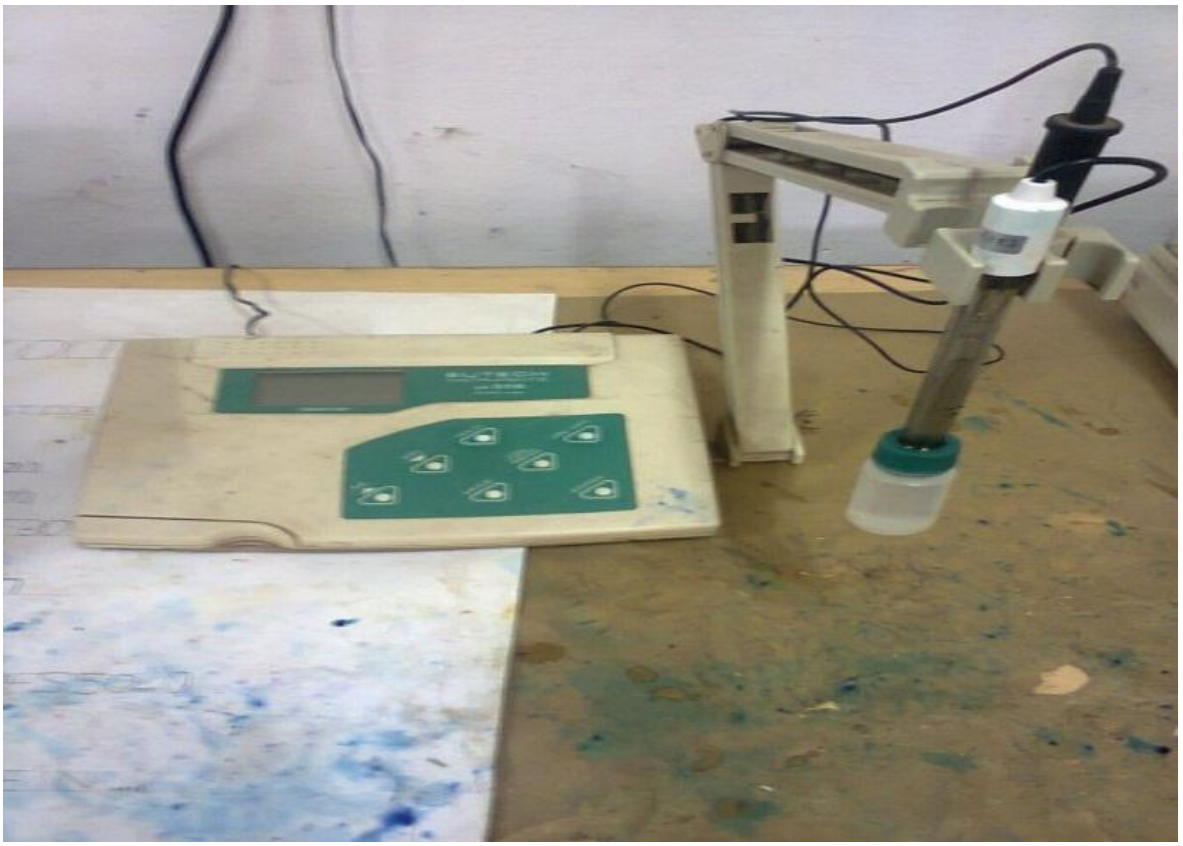


Figure 6 pH meter used to determine the solution pH

3.4 EXPERIMENTAL WORK

3.4.1 CONTACT TIME STUDY

A solution of methylene blue having concentration of 20 mg/l was prepared. 0.6 gm. of activated carbon sample was taken in a 100 ml conical flask along 100 ml of the prepared methylene blue solution. This was then kept in a shaker at a temperature of 35° C (room temperature) and vibrating at 115 rpm.

So 5 samples of above said concentration was prepared in 100 ml taken in 5 different conical fasks.

The contact time for 5 different conical flasks were taken as 20,30,40,50 & 60 min.

The % absorbance of UV at 664 nm was determined for the samples.

3.4.2 EFFECT OF pH OF THE SOLUTION

Methylene blue solution of concentration of 20 ppm but of pH varying as 1,4,6,8 and 10 were prepared. 0.6 gm of activated carbon was taken as adsorbent dose for the 100 ml solutions prepared. Contact time taken as 50 min was taken in each of the 5 conical flask of the above said concentration. The ph was maintained by adding required amount of 1 N NaOH to maintain basic in nature & 1 N H_2SO_4 to maintain acidic in nature.

The % absorbance at 664 nm was found out using a UV-spectrophotometer,

3.4.3 EFFECT OF ADSORBENT DOSAGE

The various concentration of adsorbent was taken in a 100 ml conical flask. Methylene blue concentration of 20 ppm was taken in that 100 ml conical flask The flask was put in a shaker at 115 rpm and 35 °C. Various amounts of concentration of adsorbent was taken inside 5 different conical flasks of 0.2, 0.4, 0.6, 0.8 & 1 gm respectively.

Samples were kept in each conical flask for a period of 40 min. The % absorbance at 664 nm was found out using a UV-spectrophotometer.

3.4.4 EFFECT OF CONCENTRATION OF METHYLENE BLUE

100 ml of Methylene blue solution of concentrations 20 ppm, 40 ppm, 60 ppm, 80 ppm & 100 ppm were taken in 5 different conical flasks, to which 0.6 gm of raw sample was added and shaken in a shaker at 115 rpm and 35 °C. The experiment was repeated for 1 gm of prepared sample.

Samples were collected at regular intervals for 50 minutes. The % absorbance at 670 nm was found out using a UV-spectrophotometer.

3.4.5 ADSORPTION ISOTHERM STUDIES

100 ml of methylene blue solution of concentrations 20 ppm, 40 ppm, 60 ppm, 80 ppm and 100 pm were prepared. 0.6 gm of the prepared sample was taken in conical flasks containing the solutions. The flasks were shaken at ph 5, 115 rpm and 35° C for 60 minutes. At the end of 60 minutes, samples were collected from each flasks and % absorbance of UV at 664nm was determined using a spectrophotometer.

CHAPTER 4

RESULTS AND DISCUSSIONS

4. RESULTS AND DISCUSSIONS

4.1 PROXIMATE ANALYSIS

The proximate analysis of the samples yielded the following results

Table-2 **proximate analysis of the samples.**

Moisture (%)	9.22
Ash Content (%)	1.50
Volatile Matter Content (%)	7.358
Fixed Carbon	81.922

4.2 BULK DENSITY

The bulk density of the sample was found to be =0.4512 g/ml=451.2 kg/m^3.

4.3 BET SURFACE AREA

Table 3 **BET surface area data**

Surface Area of raw activated carbon	1000.12 m^2/g

4.4 SEM

Already the images were illustrated in fig 1 (a) & (b) & fig 2 (a) & (b) above for both SEM & BSM for different wavelengths**.**

4.5 pH

pH was obtained as 10.9 which shows basic in nature.

4.6 IODINE NUMBER

The iodine no was estimated as986 mg/g.

4.7 CALIBRATION PLOT

The calibration plot for methylene blue at 664 nm was obtained as follows

Table 4 calibration data

Concentration(x) in mg/l	Absorbance(y) in %
1	0.191
2	0.382
3	0.573
4	0.764
5	0.955

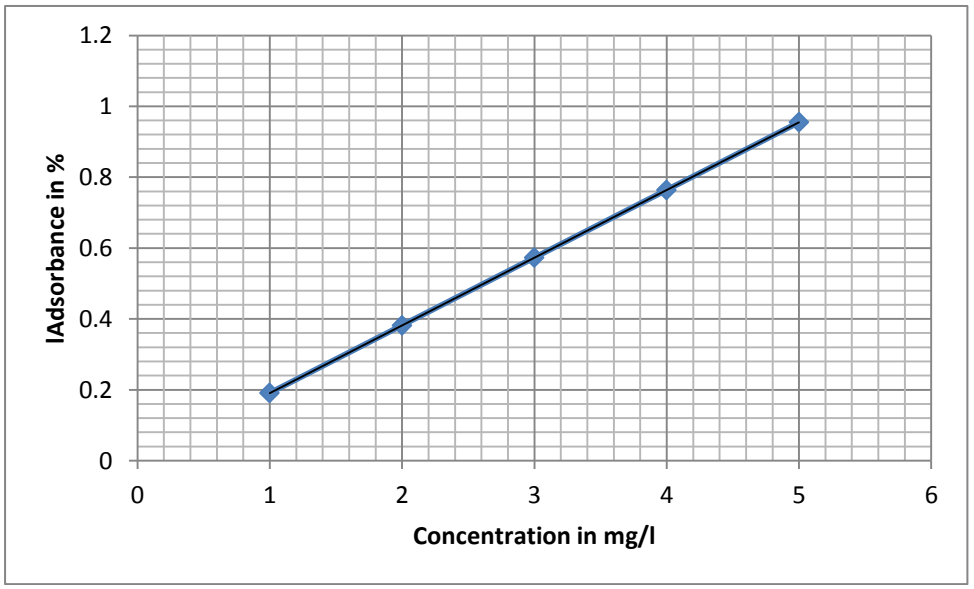


Figure 7 calibration plot Absorbance in % (y) vs concentration in mg/l (x)

From the graph the slope was found to be 0.191. Thus, equilibrium concentration at time 't', C_e= (absorbance)/(0.191)

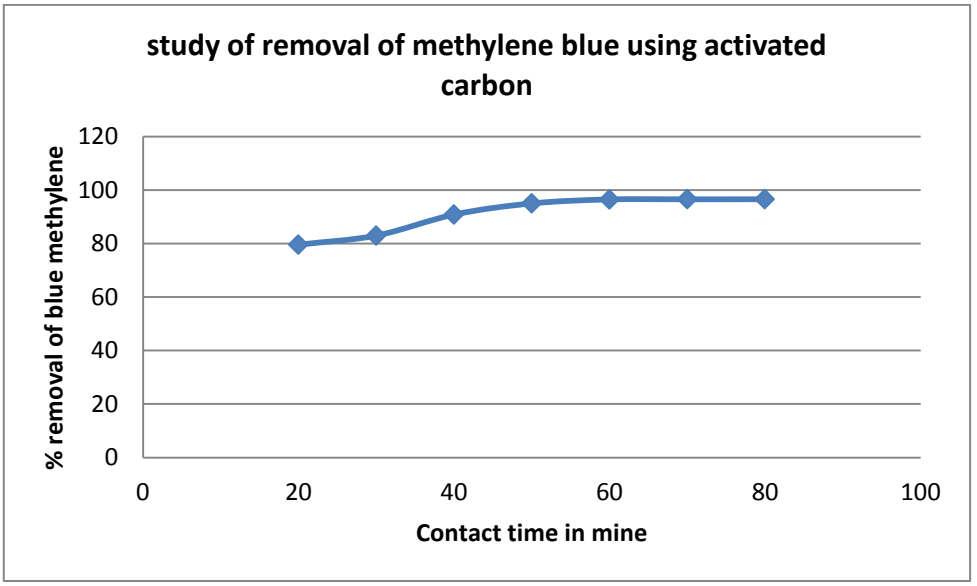
4.8 Influence of contact time on dye removal

The dependence of adsorption on contact time was studied using fixed amount (0.6g) of adsorbent (activated carbon) on 20 ppm methylene blue solution in a fixed volume (100 ml). It

was observed that adsorption increases with increase in contact time. Initially within first 10 min exponential increase in adsorption was reflected till maximum slope reached in next 10 min. There after a steady state equilibrium was obtained after a very long time.

Table 5-Contact time study data for raw sample

Time in (min)	% adsorption at 664 (nm)	% removal of blue methylene
20	0.78	79.580
30	0.65	82.984
40	0.35	90.838
50	0.191	95.00
60	0.134	96.492
70	0.132	96.54
80	0.131	96.56



4.9 Influence of Initial pH on dye removal

The effect of variation of pH on adsorption rates were studied from the data and the graph obtained between % removal of methylene blue(y) vs. pH(x).

Table 6 **effect of pH and % removal of methylene blue**

pH	adsorbance	%removal of methylene blue
1	0.31	91.88
4	0.021	99.45
6	0.024	99.37
8	0.38	95.05
10	0.6	94.29

The reason for choosing these pH values were that from the literature it was evident that the adsorption of methylene blue was highest in the natural range. Lower % removal of methylene blue at acidic pH was probably due to H^+ ions competing with the cationic charge of dye solution for adsorption on activation sites of activated carbon. Same can be explained for basic medium. The optimum pH was found to be at 5.

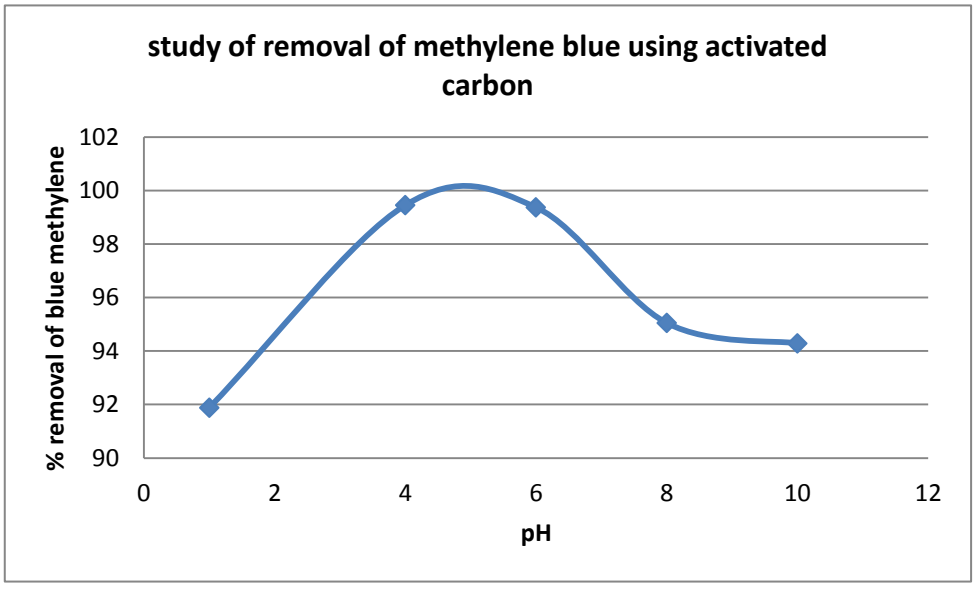


Figure 9 **% removal of methylene blue(y) vs pH (x)**

4.10 Influence of initial adsorbent dosage on dye removal

The amount of adsorbent dosage was varied in the given range 0.2 gm, 0.4 gm, 0.6 gm, 0.8 gm & 1 gm. It was observed from the graphs that increasing the dosage increases the % removal of methylene blue. As there was no drastic increase in the adsorption rate on increasing the dosage of adsorbent beyond 0.6 gm of activated carbon, hence, from economic point of view, 0.6 gm was taken as optimum dosage for removal of methylene blue.

It can be attributed to the increase in adsorbent sites for more adsorption of the dye at the fixed 20 ppm.

Table 7 **variation of % removal of methylene blue with dosage of adsorbent**

Dosage of the sample, gm	adsorbance	% removal of methylene blue
0.2	1.72	54.97
0.4	0.760	80.105
0.6	0.191	95
0.8	0.178	95.34
1.0	0.113	97.04

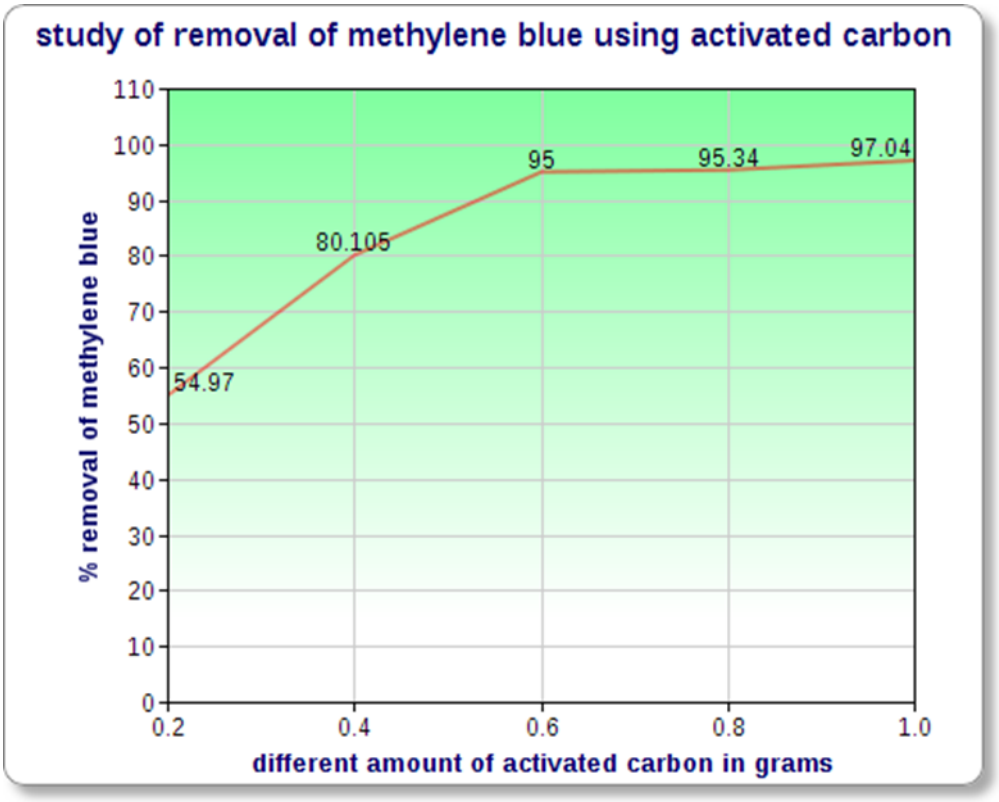


Figure 10 **% removal of methylene blue vs. dosage of the adsorbent**

4.11 Influence of initial dye concentration on dye removal

The adsorption of methylene blue onto the activated carbon was studied for different concentrations 20ppm, 40ppm, 60ppm, 80ppm and 100 ppm of methylene blue solution. The data obtained are provided in the table 8.The experiment was conducted at optimum condition 0.6 gm adsorbent dosage, 35 °C and 5 pH for contact time of 50 min. Maximum dye removal occured for low initial concentration of methylene blue that showed gradual reduction when initial concentration of Methylene blue was raised. It could be ascribed to fixed concentration

of adsorbent dosage. With increase in initial dye concentration the adsorption sites were fixed and achieved saturation at low dye concentration. Hence with increase in dye concentration no further adsorption could be achieved and resulted in reduced removal of dye with increase in dye concentration.

Table 8. % removal of blue methylene for different concentrations of MB

Methylene Blue Concentration in (mg/l)	Stock solution Adsorbance (before Shaking)	Stock solution Adsorbance (after Shaking)	% removal of Blue Methylene
2	**3.82**	**0.191**	**95**
4	**6.74**	**0.61**	**90.95**
6	**9.70**	**1.227**	**87.35**
8	**11.49**	**2.624**	**77.163**
10	**14.20**	**3.983**	**71.950**

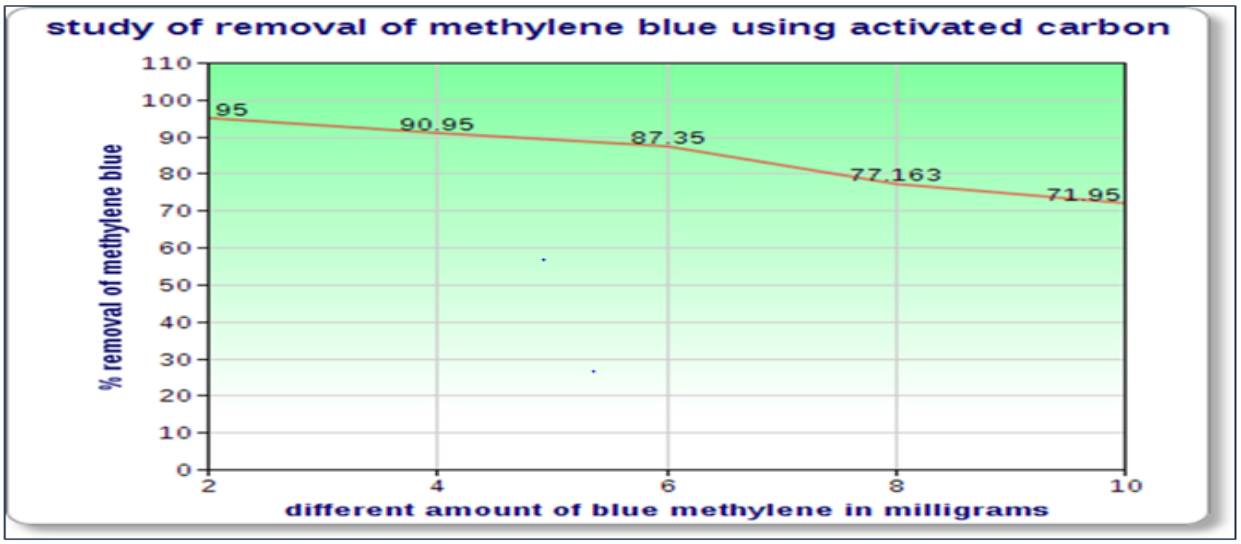


Figure 11 **% removal of methylene blue vs different amount of blue methylene in ppm**

4.12 ADSORPTION ISOTHERMS

Isotherms give an equilibrium relationship between the amounts of adsorbate adsorbed on the adsorbent surface and its concentration in the solution at a constant temperature. Numerous adsorption models are available in the literature to fit the experimental adsorption data. In this study, the data were fitted using Langmuir and Freundlich models. Each of the these models makes use of a parameter qe (i.e. adsorption capacity per unit mass of the adsorbent at equilibrium) in mg/g

$qe= (C_0-C_e)V/X$

C_0=Initial concentration of solution (mg/l)

C_e=Equilibrium concentration of solution in (mg/l)

V=Volume of solution in l

X=Amount of adsorbent used in g

4.12.1 LANGMUIR ISOTHERM MODEL

Isotherms give an equilibrium relationship between the amounts of adsorbate adsorbed on the adsorbent surface and its concentration in the solution at a constant temperature. Numerous adsorption models are available in the literature to fit the experimental adsorption data. In this study, the data were fitted using Langmuir and Freundlich adsorption models. Each of the two models makes use of a parameter Qe (i.e. adsorption capacity per unit mass of the adsorbent at equilibrium). $Q_e = (C_0 - C_e)\ V/X$

C_0=Initial concentration of solution

Ce=Equilibrium concentration of solution

V=Volume of solution

X=Amount of adsorbent used

The linear form of Langmuir expression:

$C_e/q_e = Ce/Q_o + 1/(bQ_o)$

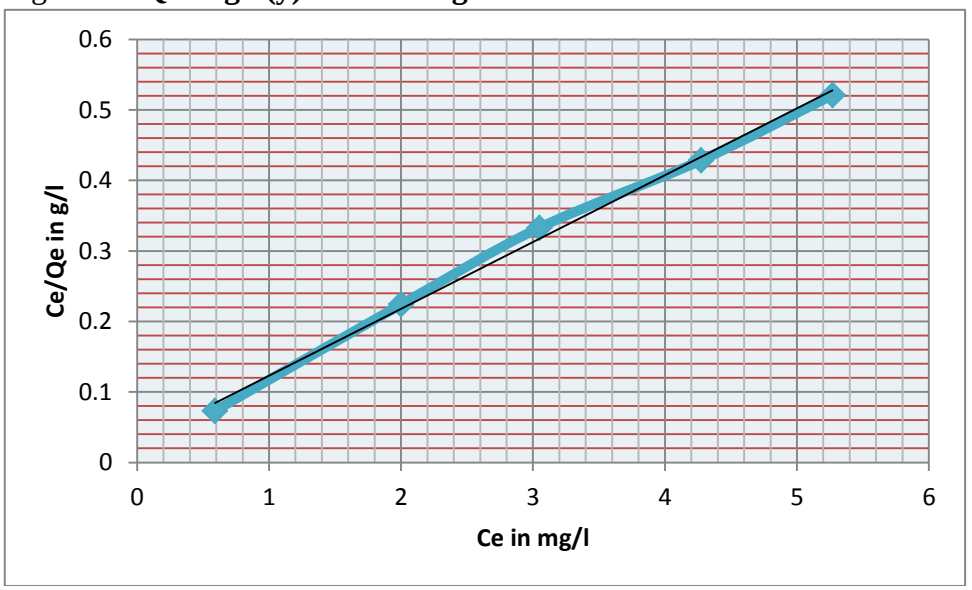
Where C_e is the equilibrium concentration of dye solution (mg/L), q_e is the equilibrium capacity of dye on the adsorbent (mg/g), Q_o is the monolayer adsorption capacity of the adsorbent (mg /g), and b is the Langmuir adsorption constant (L/mg) and is related to the free energy of adsorption.Langmuir model was fitted to the experimental data as shown in the figure below.The activated carbon was taken as 0.6 gm for different concentration of methylene blue. The solution inside the conical flask was maintained around pH 5 & it was kept in shaker for 60 min.

Concentration in mg/l	absorbance	Before original absorbance	Co in mg/l	Ce in mg/l	Qe in mg/g	Ce/Qe
20	0.093	7.71	48.952	0.590	8.060	0.0732
40	0.315	7.89	50.095	2	8.919	0.224
60	0.48	8.19	52	3.048	9.159	0.;3328
80	0.673	10.1	64.127	4.273	9.976	0.4283

100	0.83	10.4	66.032	5.27	10.127	0.521

Table 9 tabulation for Langmuir isotherm

Fig-12 **Ce/Qe in g/l (y) vs Ce in mg/l**



Form the graph, the slope was found to be 0.7765 which gives us the value of $1/(bQ_o)$.

The equation is y=0.0957*x +0.017

The y-axis intercept gives the $1/Q_o$= 0.0957

Thus Q_o=10.45 mg and b=5.629 l/mg; R^2=0.999

4.12.2 FREUNDLICH ISOTHERM MODEL

The Freundlich model is based on the assumption that metal ions are adsorbed on a heterogeneous surface and is not restricted to formation of monomolecular layer.

The linear form can be written as:

$\ln qe = \ln k_f + (1/n)*\ln Ce$

where, k_f and n (dimensionless constants) are the Freundlich adsorption isotherm constants, which indicates the capacity and intensity of the adsorption, respectively.

The Freundlich model was fitted to the experimental data as shown below

Table 10 **log Qe (y) vs log Ce (x) for freundlich isotherm**

Log Qe	Log Ce
0.906	-0.229
0.950	0.301
0.962	0.484
0.999	0.631
1.005	0.722

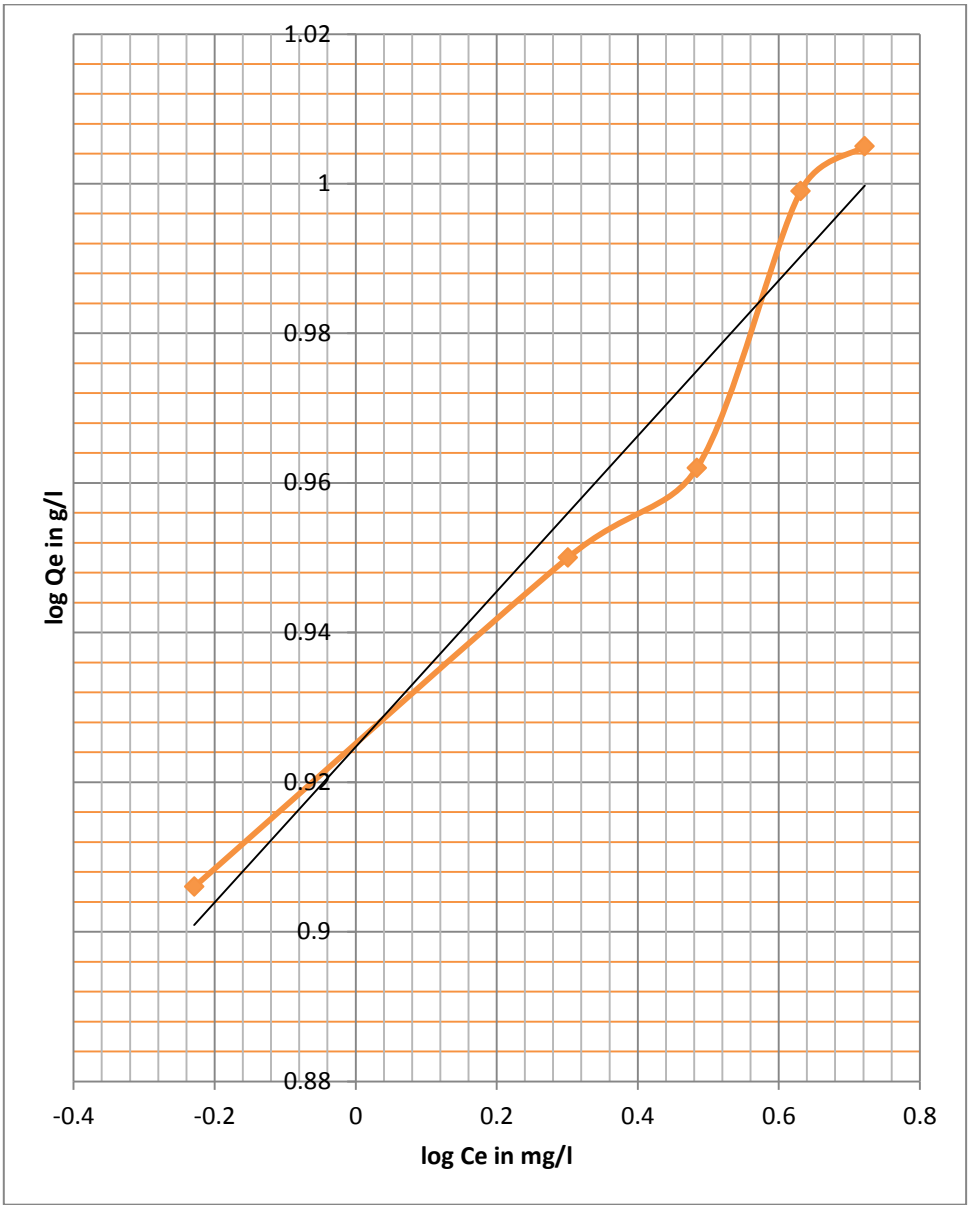


Figure 13 Freundlich model

From the graph the value of n was found to be 9.615 and k_f was found to be 8.511
The equation is

y= 0.104*x +0.93 and R^2=0.948

Since the R^2 are fairly close to 1, thus both the models describe the system well but Langmuir isotherm model was preferred.

Table 11 **Comparision of different adsorbents for methylene blue dye adsorption capacity**

Raw materials	**C_o,initial concentration, mg/l**	**q_e, mg/g**	**References**
Our study(coconut shell activated carbon)	100	10.127	-
Walnut shells	100	3.53	Aygün A. ,Yenisoy-Karakaş S. [9]
Coir pith	100	5.8	Kavitha D. , Namasivayam C. [10]
Apricot stones	100	4.1	Aygün A. , Yenisoy-Karakaş S. [9]
Almond shell	100	1.3	Aygün A. ,Yenisoy-Karakaş S. [9]
Hazelnut shell	100	8.82	Aygün A. ,Yenisoy-Karakaş S. [9]
Silk cotton hull	100	2.40	Kadirvelu K., Kavipriya M. [11]
Maize cob	100	5.00	Kadirvelu K., Kavipriya M. [11]
Coconut coir dust	100	15.25	Macedo J. S., Júnior N. B., Almeida L. E. [12]
Banana pith	100	4.67	Kadirvelu K., Kavipriya M. [11]

CHAPTER 5
CONCLUSIONS

5. CONCLUSION

Here we conducted many characterization techniques like Proximate Analysis, Scanning Electron Microscope (SEM), pH, Porosity, BET surface area, Iodine Number & Methylene Blue

Through pH we were able to predict that the given sample of activated carbon is of basic in nature.

Through SEM we could predict the composition of the given activated carbon.
It is almost made up of pure carbon (99%). Platinum is added as a coating material for SEM analysis.

From the contact time studies, it was seen that % removal of blue methylene for 1^{st} 10 min increases but for next 10 minutes, the slope gets further increase & thereafter slope gets decrease for next 10 min & finally attains a steady value after a very long time This trend can be attributed .to the fact that as the contact time increases more is the adsorbate-adsorbent interaction & thus leads to more adsorption & hence % removal of MB also gets raised with respect to increase in contact time.

For pH, % removal of methylene blue remains lowest in both acidic & basic medium & it occurs maximum in neutral medium. This can be accounted because in acidic medium due to high H^+ concentration, there is a repulsion of H^+ ion with cationic charge of dye for which the adsorption can't takes place suitably as in comparison to neutral medium.

For adsorbent dosage, it was seen that % removal of methylene blue increases with increase in adsorbent dosage. This trend can be attributed because of more dosage, the surface area exposed to dye solutions gets more so that more dye can be adsorbed into the pores of the adsorbent hence more is the % removal of MB.

For methylene blue dosage, the % removal of MB start decreasing with respect to increase in concentration of MB. This happens due to fixed amount of adsorbent in increasing Methylene blue concentration.

For adsorption isotherm we plotted both for Langmuir & Freundlich models & it was observed that regression coefficient came close to 1. So both the models can be fitted for the data that was obtained during experiment. However Langmuir Isotherm is more accurate

because regression coefficient was R^2=0.99 as comparison to R^2=0.948 for Freundlich Isotherm.

Studying through different graphs of pH, contact time, adsorbent concentration & Methylene Blue concentration we got optimum values for each case as

pH= 5; Contact time= 5 0 min; Adsorbent dosage= 0.6 gm; Methylene blue concentration= 20 mg/l

Hence after carrying out rigorous experiments we finally came to conclusion that activated carbon prepared from coconut shell can be effectively used for the removal of methylene blue effectively conducted at the optimum process condition.

CHAPTER 6
REFERENCES

REFERENCES

1. Dash Bibek. Competitive Adsorption of dyes (congo red, methylene blue, malachite green) on Activated Carbon, B.tech thesis. ethesis.nitrkl.ac.in 2010.
2. Dalia Khalid,et.al, Batch adsorption of basic dye using acid treated kenaf fibre char: Equilibrium, kinetic and thermodynamic studies,2011.
3. FaradillaBintiLokman. Dye removal from simulated wastewater by using empty fruit bunch as an adsorbent agent, 2006.
4. Ioannidis et.al, "Agricultural residues as precursors for activated carbon production—A review ", Renewable and Sustainable Energy Reviews 11 (2007) 1966–2005.
5. Adinata et.al, "Preparation and characterization of activated carbon from palm shell by chemical activation with K_2CO_3", Bioresource Technology, 98, (2007), pp. 145–149.
6. Senthilkumaar et.al, "Adsorption of methylene blue onto jute fiber carbon: kinetics and equilibrium studies.", Journal of Colloid and Interface Science (2005) Volume: 284, Issue: 1, Pages: 78-82
7. Hameedet.al, "Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust" , Dyes and Pigments (2007) Volume: 75, Issue: 1, Pages: 143-149
8. Hameedet.al, "Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies", Journal of Hazardous Materials (2007), Volume: 141, Issue: 3, Publisher: Elsevier Science BV, Pages: 819-825
9. A. Aygün, et.al, "Production of granular activated carbon from fruit stones and nutshellsand evaluation of their physical, chemical and adsorptionproperties," Microporous and Mesoporous Materials, vol. 66, no.2-3, pp. 189–195, 2003.
10. D. Kavitha and C. Namasivayam, "Experimental and kineticstudies on methylene blue adsorption by coir pith carbon," Bioresource Technology, vol. 98, no. 1, pp. 14–21, 2007.
11. K. Kadirvelu, et.al, "Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions," Bioresource Technology, vol. 87, no. 1, pp. 129–132, 2003.
12. J. S. Macedo, N. B. Júnior, L. E. Almeida et al., "Kinetic and calorimetric study of the

adsorption of dyes on mesoporous activated carbon prepared from coconut coir dust," Journal of Colloid and Interface Science, vol. 298, no. 2, pp. 515–522, 2006.

13. Caturla F., et.al. Preparation of activated carbon by chemical activation with ZnCl2, Carbon, 29 (1991): pp. 999-1007.
14. Girgis B.S., et.al. Activated carbon from sugar cane bagasse by carbonization in the presence of inorganic acids, Journal of Chemical Technology and Biotechnology, 61 (1994): pp. 87-92.
15. Hu Z., Vansant E.F. Synthesis and characterization of a controlled-micropore-size carbonaceous adsorbent produced from walnut shell, Microporous Materials, 3 (1995): pp. 603-612.
16. Avomj. et.al. Adsorption f methylene blue from an aqueous solution on to activated carbon from palm-tree cobs.Carbon Volume 35, Issue 3, 1997, Pages 365–369
17. Shawabkeh R. A., et.al. Adsorption of phenol and methylene blue by activated carbon from pecan shells,2007.
18. Yasin Y. et.al. adsorption of methylene blue onto treated activated carbon.The Malaysian Journal of Analytical Sciences, Vol 11, No 11 (2007): page 400 – 406
19. Ozer A. et.al, Removal of methylene blue from aqueous solution by dehydrated wheat bran carbon. J Hazard Mater. 2007 Jul 19;146(1-2):262-9
20. Langmuir, I. The constitution and fundamental properties of solids and liquids. parti. solids.Journal of the American Chemical Society, 1916, 38 (11): 2221–2295.
21. Parashar C. .Removal of Malachite Green dye by adsorption using char. B.tech thesis ethesis.nitrkl.ac.in, 2012.
22. Pati S. R..Synthesis and characterisation of activated carbon andits study on Cr (VI) removal from water. B.tech thesis ethesis.nitrkl.ac.in, 2012.
23. Brunauer S., Emmett P. H., Teller E. Adsorption of Gases in Multimolecular Layers, Journal of American Chemical Society, 60(1938): pp. 309–319
24. Freundlich H.Z. Over The Adsorption in Solution, Journal of Physical Chemistry, 57(1906): pp. 385-470.
25. Amankwah.K.A.G,Schwarz.J.K., "*A modified approach for estimating pseudo-vapor pressure in the application of the Dubinin-Astakhov equation*" Carbon .,33 (1995) :pp
26. . Chakraborty.A, Saha.B.B, Ng.K.C, Koyama.S, Srinivasan .K "*Theoretical Insight of Physical Adsorption for a Single Component Adsorbent +Adsorbate System: I. Thermodynamic Property Surfaces*" Langmuir., 25 (2009) :pp.2204-2211.

27. D.D. Do, Nicholson. D, Do. H.D "*On the Henry constant and isosteric heat at zero loading in gas phase adsorption*" Journal of Colloid and Interface Science.,324 (2008):pp 15-24.

28. Huang.C.C, Chen.H.M, Chen.C.H "*Hydrogen adsorption on modified activated carbon*" International Journal of Hydrogen Energy.,35(2010): pp 2770-2780

29. Keller .J.U ,Staudt.R,Siegen.U ., "*Gas adsorption equilibria experimental method and adsorptive isotherms*". Germany, Springer, 2005

30. . Ming .H.J., "*Adsorption evaporative emission control system for vehicles*". National university of Singapore, PH.D Thesis, 2009

31. Yang, R.T.,*Gas separation by adsorption*. Boston, Butterworth Publishers, 1987

32. Saha.B.B, Habib.K , Ibrahim.I, Sharkawy.El, Koyama.S "*Adsorption characteristics and heat of adsorption measurements of R-134a on activated carbon*" International journal of refrigeration .,32 (2009) :pp1563-1569.